



# An Atmospheric Atomic Oxygen Source for Cleaning Smoke Damaged Art Objects

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# AN ATMOSPHERIC ATOMIC OXYGEN SOURCE FOR CLEANING SMOKE DAMAGED ART OBJECTS

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## SUMMARY

Soot and other carbonaceous combustion products deposited on the surfaces of porous ceramic, stone, ivory and paper can be difficult to remove and can have potentially unsatisfactory results using wet chemical and/or abrasive cleaning techniques. An atomic oxygen source which operates in air at atmospheric pressure, using a mixture of oxygen and helium, has been developed to produce an atomic oxygen beam which is highly effective in oxidizing soot deposited on surfaces by burning candles made of paraffin, oil or rendered animal fat. Atomic oxygen source operating conditions and the results of cleaning soot from paper, gesso, ivory, limestone and water color-painted limestone are presented.

## 1.0 INTRODUCTION

The National Aeronautics and Space Administration has maintained an interest in the effects of atomic oxygen interaction with materials, because spacecraft in low Earth orbit are subjected to attack by environmental atomic oxygen formed by photodissociation of diatomic oxygen in the Earth's upper atmosphere. The need to assess atomic oxygen durability of low Earth orbital spacecraft materials has prompted the development of many types of atomic oxygen sources used for simulation of the degradation effects of materials in low Earth orbit. Although almost all low Earth orbital atomic oxygen simulation facilities require the materials exposed to be in a vacuum environment, atomic oxygen can be produced at atmospheric pressures under suitable conditions (ref. 1).

The general awareness that atomic oxygen could readily oxidize carbon and hydrocarbon materials has prompted the evaluation of its use for the removal of soot and other carbonaceous contaminants from the surfaces of fire damaged paintings (refs. 2 to 4). Interest in the use of atomic oxygen to remove soot or other organic contaminants from the surfaces of paintings and other objects, combined with the desire to perform such removal processes at atmospheric pressures as opposed to in vacuum, has encouraged the development of an atmospheric atomic oxygen beam system, which is the subject of this paper (ref. 5).

## 2.0 APPARATUS AND PROCEDURE

### 2.1 Atmospheric Atomic Oxygen Source

The atmospheric atomic oxygen source (AAOS) described in this paper employs a high voltage, low current, DC arc to dissociate diatomic oxygen ( $O_2$ ) and produces atomic oxygen (O) and ionic oxygen ( $O^+$ ) in a helium rich background environment. A schematic diagram of the AAOS is shown in figure 1.

The DC arc is formed by an anode needle and cathode orifice. Positive oxygen ions are produced in the arc discharge and are attracted towards the negative cathode orifice plate causing the arc to pass axially through the orifice and then back toward the orifice plate. This causes a stream of oxygen ions and charge exchange energetic atomic oxygen atoms to emerge which fail to make the  $180^\circ$  bend to return to the cathode orifice plate. The resultant

stream of atomic and ionic oxygen atoms can travel up to approximately 1 cm downstream of the orifice plate when the cathode has a 7 kV DC bias and a current limiting resistor of 1 MW is used as shown in figure 1. Under such conditions, arc currents of approximately 5 to 6 mA are attained. For the cathode orifices evaluated in this paper, typical cathode orifice plate thicknesses were 0.38 mm.

The AAOS anode needle is a sharpened 300 series stainless steel wire approximately 1.6 mm in diameter. A typical anode needle tip is located 2 to 4 mm from the upstream side of the cathode orifice plate. The anode needle is isolated from the orifice plate by means of an electrically insulating cylinder. Within this cylinder a mixture of oxygen and helium is introduced and forced out the cathode orifice. The purpose of the helium is to separate the atomic oxygen atoms to reduce the probability of their recombination.

An overall photograph of the AAOS and its associated power supply and resistor bank are shown in figure 2. Because the AAOS does produce some ozone ( $O_3$ ), the source is operated in a fume hood or other ventilation system to safely remove the ozone. A close-up picture of the AAOS is shown in figure 3. As can be seen in figure 3, the cathode orifice plate is in the shape of a truncated cone (funnel shape) to allow ease of viewing of surfaces during exposure to atomic oxygen.

## 2.2 Smoke Deposition

Three types of smoke deposition were used to evaluate the effectiveness of the AAOS to clean away soot. The first smoke deposition technique was to deposit paraffin candle soot on paper, ivory and limestone. Candle smoke was also applied to limestone which had been painted with water colors.

Because the deposition of candle smoke was difficult to produce in a spatially homogenous manner, a second smoke deposition system was designed and constructed which allowed a uniform smoke deposit to be applied to gesso coated canvas and paper substrates. This system deposited soot by means of burning a 4 in. wide by 1 in. thick cotton cloth wick which was soaked in 10W40 motor oil. Smoke from the wick was allowed to rise and deposit onto a circular carousel of samples attached to standard microscope glass slides. During a typical smoke deposition exercise, the carousel (fig. 4) rotated many times, in a horizontal plane, to allow uniform deposition of smoke on each sample.

Because oil flames tend to flicker in the presence of wind, thus causing irregular smoke deposition, the oil flame smoke deposition system was enclosed in a metal cylinder to minimize flame flickering (see fig. 5). This system was used to deposit uniformly thick coatings of smoke soot onto multiple substrates. Samples produced with this deposition technique were used to optimize the AAOS operating parameters.

The third smoke deposition technique deposited soot from a candle made of rendered animal fat. This type of candle was used to deposit soot similar to what is expected to be found on old art objects which may have been exposed to lamps made using rendered animal fat. The rendered fat candle soot was deposited in a manner identical to the paraffin candle soot with samples being placed over the flame and moved as needed to deposit an opaque black smoke deposit.

Measurement of the degree of atomic oxygen cleaning on white substrates was performed using a diffuse incandescent white light reflectance measurement system or a laser reflectance measurement system as shown in figure 6. The 670 nm wavelength laser reflectance measurement system illuminates samples at approximately  $45^\circ$  from normal incidence. Measurements were made of both specular and diffuse reflectance by means of photodiodes located as shown in figure 6.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Optimization of Atmospheric Atomic Oxygen Source Operation

The optimum voltage and resistance for the AAOS was explored by measuring the diffuse reflectance of incandescent white light from the atomic oxygen cleaned areas of the gesso that had oil soot deposits to determine various combinations of voltage and resistance. Based on the results of these tests, shown in figure 7, a voltage of 7,000 V and a resistance of 1 MW was used for the optimum operating condition for the remainder of the tests performed. Operation of the AAOS using a 7 kV DC power supply with a 1 MW resistance, produced approximately a 6 mA arc which was stable.

Figure 8 shows a typical paraffin candle soot deposit on paper after exposure to the atmospheric atomic oxygen beam for 30 sec. Although the AAOS will oxidize soot if operated on air or pure oxygen, it is far more effective if it is operated with a mixture of helium and oxygen. Using pieces of paper with identical deposition of soot, the optimum helium to oxygen ratio was determined as a function of the cathode orifice diameter as shown in figure 9. The optimum gas mixture was 4.0 l/min of He and 0.4 l/min of O<sub>2</sub>. The optimum cleaning was achieved with a cathode orifice of 3.1 mm in diameter, as shown in figure 10.

The effectiveness of the cleaning with respect to distance from the cathode orifice plate was measured by examining the product of the cleaned area times its reflectance (for soot on paper) as shown in figure 11. As can be seen from figure 11, the AAOS was found effective for cleaning at a distance of 4 mm from the cathode orifice plate. At distances beyond 4 mm greater durations for cleaning were required to remove soot. In addition, at very small distances the sample area cleaned was much smaller in diameter and the temperature was higher as shown in figure 12. The temperatures shown in figure 12 are for room temperature gas feed as opposed to any chilling of the helium or oxygen which should reduce the sample temperature during exposure.

### 3.2 Cleaning of Soot from Ivory

Samples of thin (<1 mm thick) ivory from piano keys were used to evaluate the effectiveness of the AAOS when cleaning paraffin candle soot from ivory substrates. A soot spot was deposited on the ivory as shown in figure 13(a). As with the removal of soot from paper, gradual oxidation of the soot was visible from 30 sec to 2 min of exposure as shown in figure 13(b). Figure 13(c) shows complete oxidation of the soot deposit from the ivory which generally occurred after a few minutes of exposure to the atomic oxygen source, depending upon the thickness of the soot. The AAOS was also evaluated for its potential to whiten ivory which had darkened as a result of the accumulation of finger oil being absorbed into the surface of the ivory and darkening over time. However, because the atmospheric atomic oxygen source reacts only with organic materials on the surface, it was found to be only slightly effective in whitening ivory darkened from finger oil. It was highly effective, however, in removing all evidence of soot from the ivory as shown in figure 14.

### 3.3 Cleaning of Soot from Limestone

Samples of limestone broken by crushing to produce a pristine but rough surface, were coated with soot from a paraffin candle flame and exposed to the AAOS to evaluate the effectiveness of cleaning on highly roughened surfaces. Figure 15 shows a typical soot coated limestone surface after exposure to the AAOS in a few selected areas. A similar evaluation of the effectiveness of the AAOS to clean soot deposited from a candle made from rendered animal fat onto the limestone was conducted and this also produced a surface which appeared completely free from any evidence of soot deposit.

Stripes of watercolor paint were applied to limestone followed by the deposition of both paraffin candle smoke soot and rendered animal fat soot. In both cases complete oxidation occurred revealing the underlying watercolor surface paint on the limestone. As can be seen in figure 16, the watercolor stripes on the limestone are unaffected by the atomic oxygen attack despite the fact that all of the paraffin candle soot was removed from the areas exposed to the atomic oxygen beam.

Functional cleaning by means of the AAOS could be accomplished by mounting the source on an x-y translation system which slowly rasters the exposure area over the soot coated area.

## 4.0 CONCLUSIONS

An atomic oxygen beam source which operates on air at atmospheric pressure using a mixture of helium and oxygen has been developed. The atomic oxygen beam is highly effective in removing soot produced by paraffin, oil and rendered animal fat candle flames. The atomic oxygen beam cleans an area of a few millimeters in diameter at a distance of up to 1 cm from the source with cleaning durations from 30 sec to several minutes depending upon the thickness of the soot. The atmospheric atomic oxygen source was used to clean soot from paper, gesso, ivory, limestone and water-color painted limestone.

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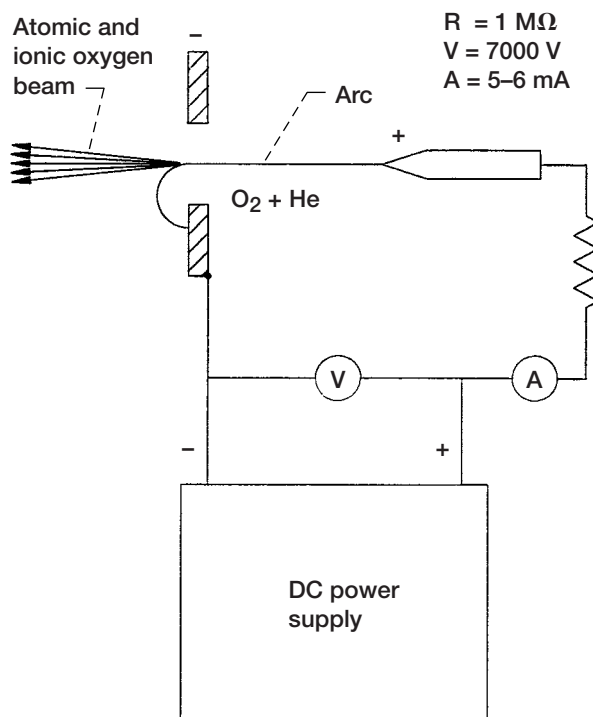


Figure 1.—Schematic diagram of atmospheric atomic oxygen source.



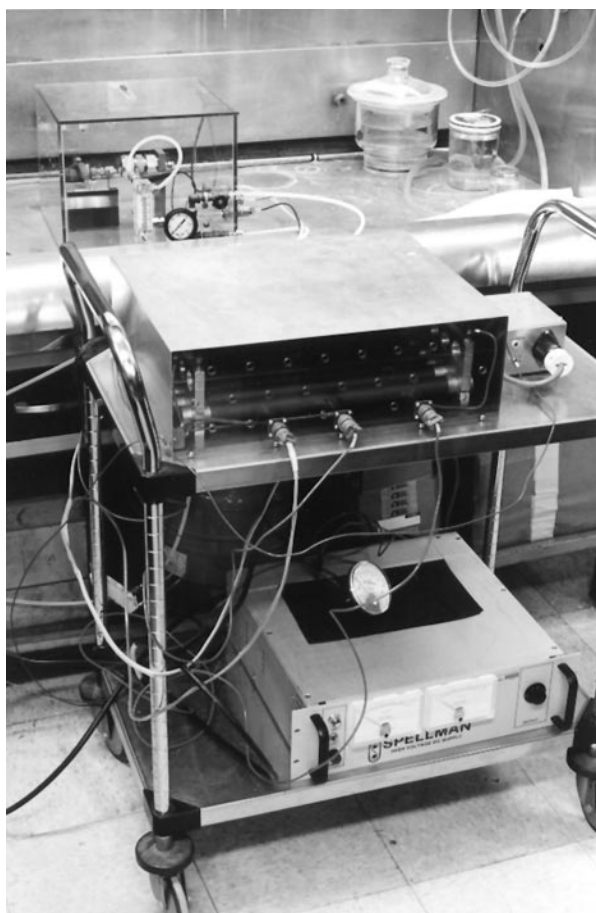


Figure 2.—Photograph of atmospheric atomic oxygen source with its power supply and resistor bank.

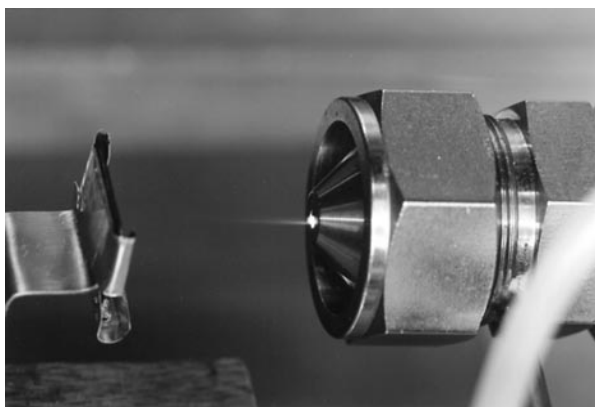


Figure 3.—Close-up photograph of atmospheric atomic oxygen source with sample holder fixture downstream of the source.



Figure 4.—Photograph of carousel used for deposition of smoke on paper samples by means of an oil-soaked cotton wick.



Figure 5.—Overall photograph of oil-smoke deposition system including wind-shield and deposition carousel.

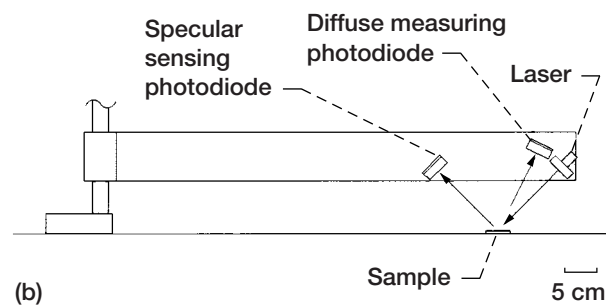
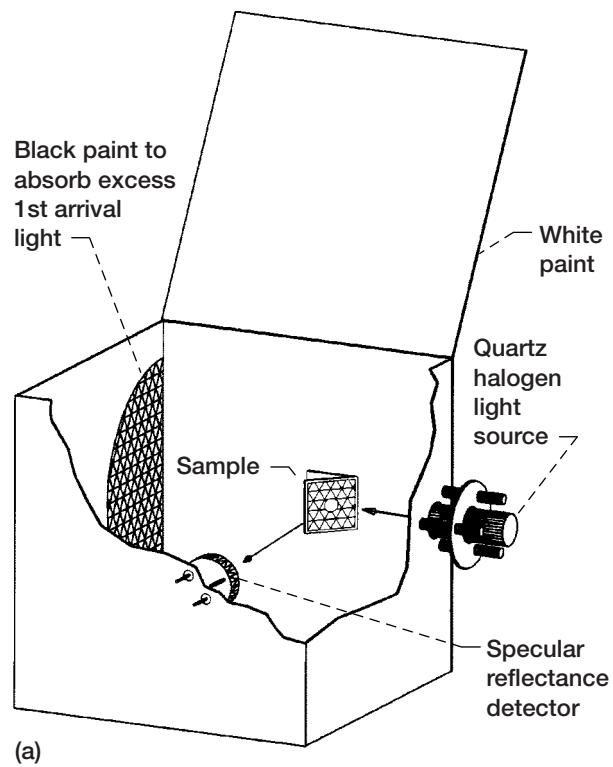


Figure 6.—Reflectance measurement systems used to measure degree of soot removed from white surfaces. (a) Diffuse white incandescent light reflectance measurement system. (b) Laser reflectance measurement system

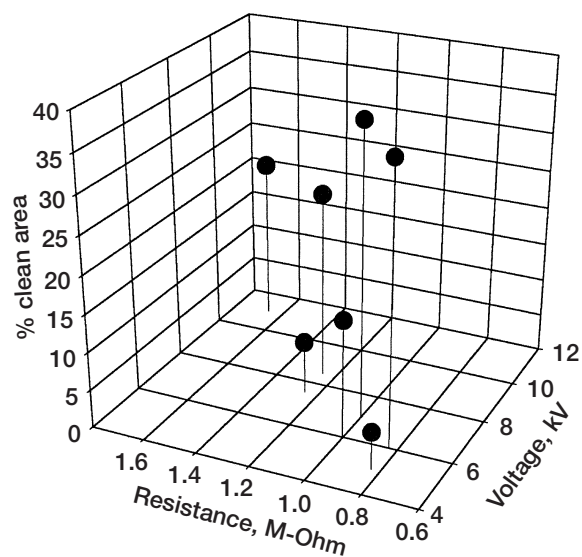


Figure 7.—Atomic oxygen cleaning effectiveness dependence on power supply voltage and resistance.

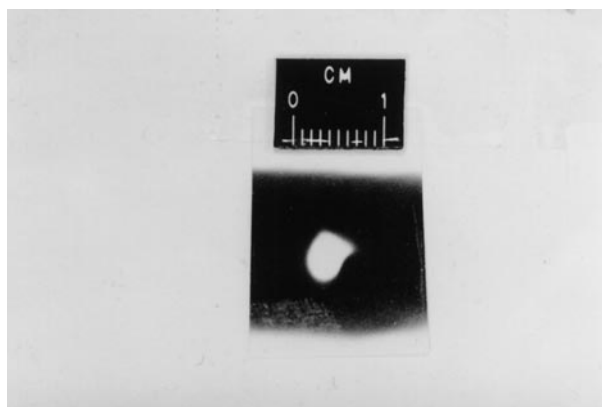


Figure 8.—Paraffin candle soot deposit on paper after exposure to the atmospheric atomic oxygen source for 30 seconds showing a white area where the soot was removed.

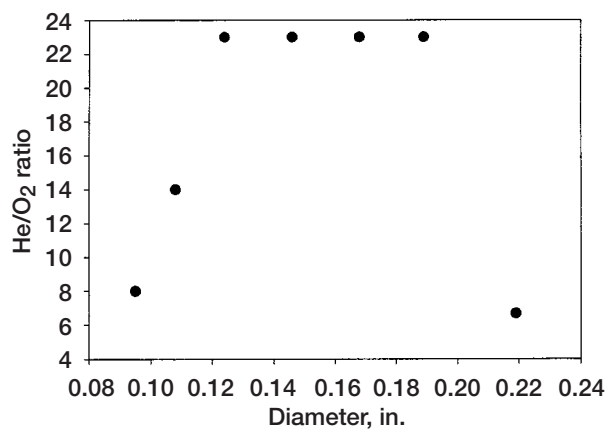


Figure 9.—Optimum helium/O<sub>2</sub> ratio as a function of cathode orifice diameter.

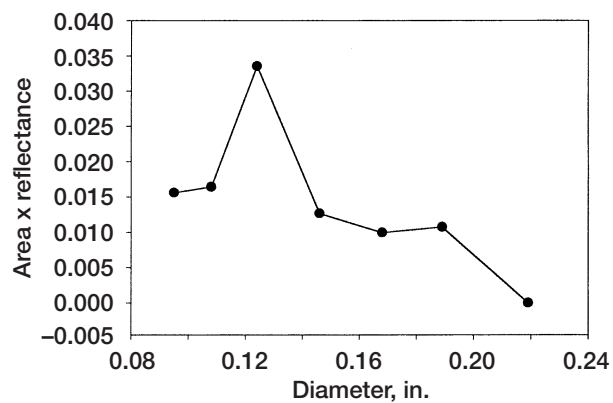


Figure 10.—Dependence of the product of cleaned area and its reflectance as a function of orifice plate diameter for candle smoke soot on paper.

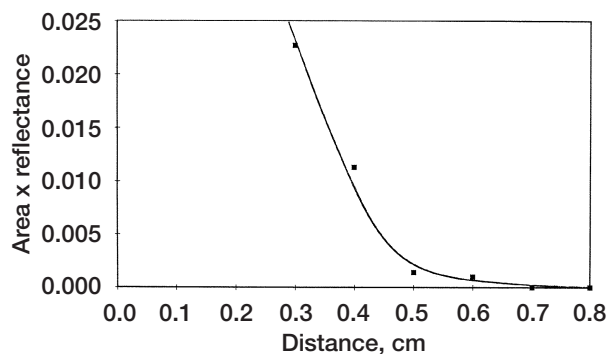


Figure 11.—Dependence of the product of cleaned area and its reflectance as a function of distance for candle smoke soot on paper.

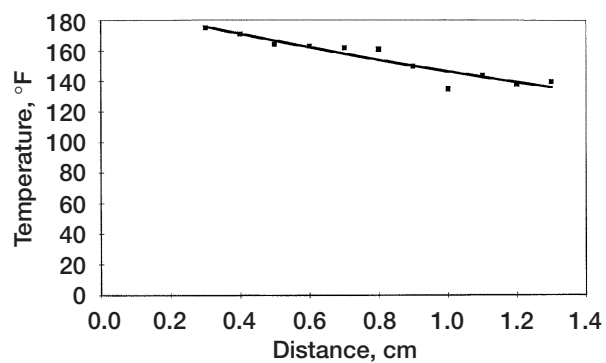


Figure 12.—Substrate temperature as a function of distance after 3 minutes of exposure to the atmospheric atomic oxygen beam.

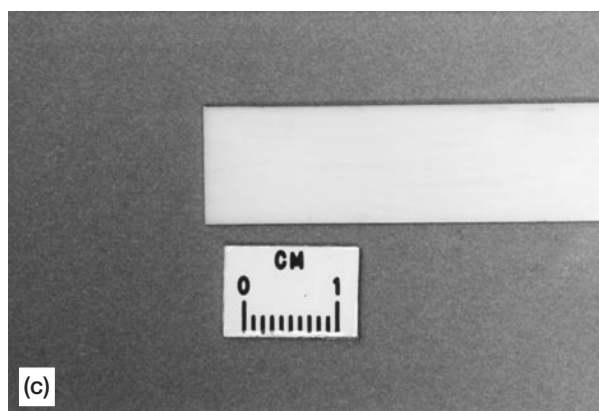
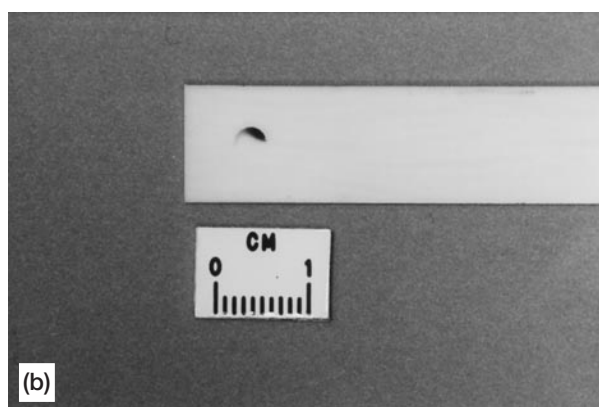
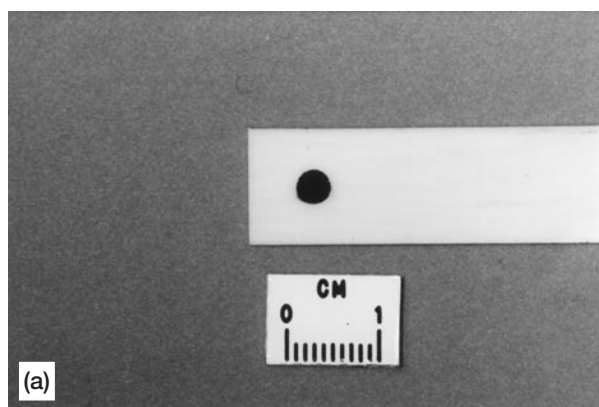


Figure 13.—Photographs of the removal of paraffin candle soot from the surface of ivory piano keys.  
 (a) Ivory piano key showing initial soot deposit.  
 (b) Partially oxidized soot spot. (c) Fully cleaned soot spot.

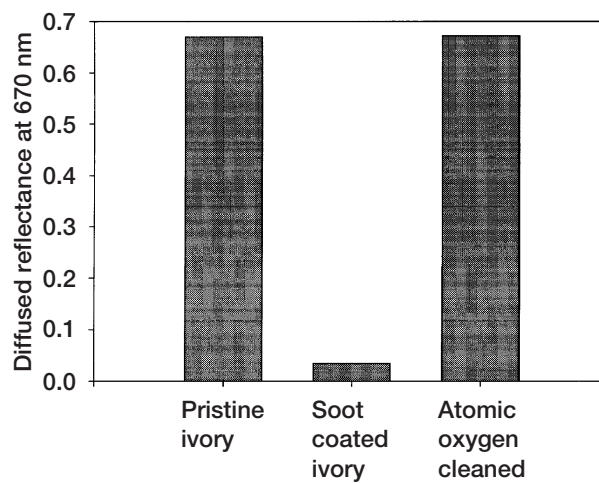


Figure 14.—Comparison of the diffuse reflectance at 670 nm for pristine, paraffin candle smoke soot coated, and atmospheric atomic oxygen source cleaned ivory.



Figure 15.—Rendered animal fat candle smoke soot coated rough limestone surface after exposure to the atmospheric atomic oxygen source.



Figure 16.—Watercolor stripes on limestone after deposition with rendered animal fat candle soot followed by atmospheric atomic oxygen source cleaning.

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